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The transition from crossite to actinolite in metabasites of the Combin unit in Vallée St. Barthélemy (Aosta, Italy).

by *Ruedi Sperlich*[1]

Abstract

Sodic amphiboles appear in different rock types of the Combin unit north of the Dora Baltea River. In epidote-rich prasinites, relics of different amphibole generations ranging from crossite to barroisite, Mg-hornblende and actinolite are preserved, and can be distinguished by their pleochroism and by textural relationships. Electron-microprobe analyses show a large compositional gap between crossite and barroisite, as found in other areas. No gap was detected within calcic amphiboles. Substitution vectors document variable compositional trends between different stages of amphibole growth. Coexisting epidotes are Fe-rich with an increase in Al from core to rim.

Comparison with similar assemblages suggests that the metamorphic evolution of the Combin unit involved early blueschist metamorphism followed by a greenschist overprint.

Keywords: Amphiboles, composition, growth stages, metamorphic evolution, Combin unit, Aosta, Italy.

Introduction

Sodic amphiboles occur in metabasites of the upper Combin unit near Aosta in northern Italy. These rocks were studied in an area located north of the Dora Baltea River 30 km south-west of Zermatt, between Valpelline and Valtournanche, covering the slopes south of St. Barthélemy, at 1200 m to 1800 m a.s.l. (see Fig. 1).

Various amphiboles occur in meta-volcanic rocks and quartzitic mica schists, some containing relics of sodic amphiboles. One sample, showing different stages of amphibole growth ranging from crossite to barroisite, hornblende and actinolite will be treated in detail.

Occurrences of blue amphiboles in Mn-rich quartzitic schists of the Combin unit have so far been reported by DAL PIAZ (1979), CABY (1981), BALDELLI et al. (1983) and BALLEVRE and KIENAST (1987). Blue amphiboles in Combin-metabasites are reported by AYRTON et al. (1982), DAL PIAZ and ERNST (1978) and ERNST and DAL PIAZ (1978), but no chemical data have been provided. The purpose of this study is to give a preliminary description of the variation in amphibole chemistry in metabasites of the Combin unit, and explore the possibility that they may well have reached P-T-conditions of the blueschist facies before undergoing greenschist metamorphism related to mesoalpine thermal equilibration. Alpine metamorphism in the Combin unit has so far been considered to be solely characterized by greenschist conditions.

Geological setting

The Piemont ophiolite nappe ('complesso piemontese dei calcescisti con pietre verdi', DAL PIAZ, 1971, 1974a, 1974b) is a complex of partially subducted remnants of an ophiolite-floored basin. It is interposed between the un-

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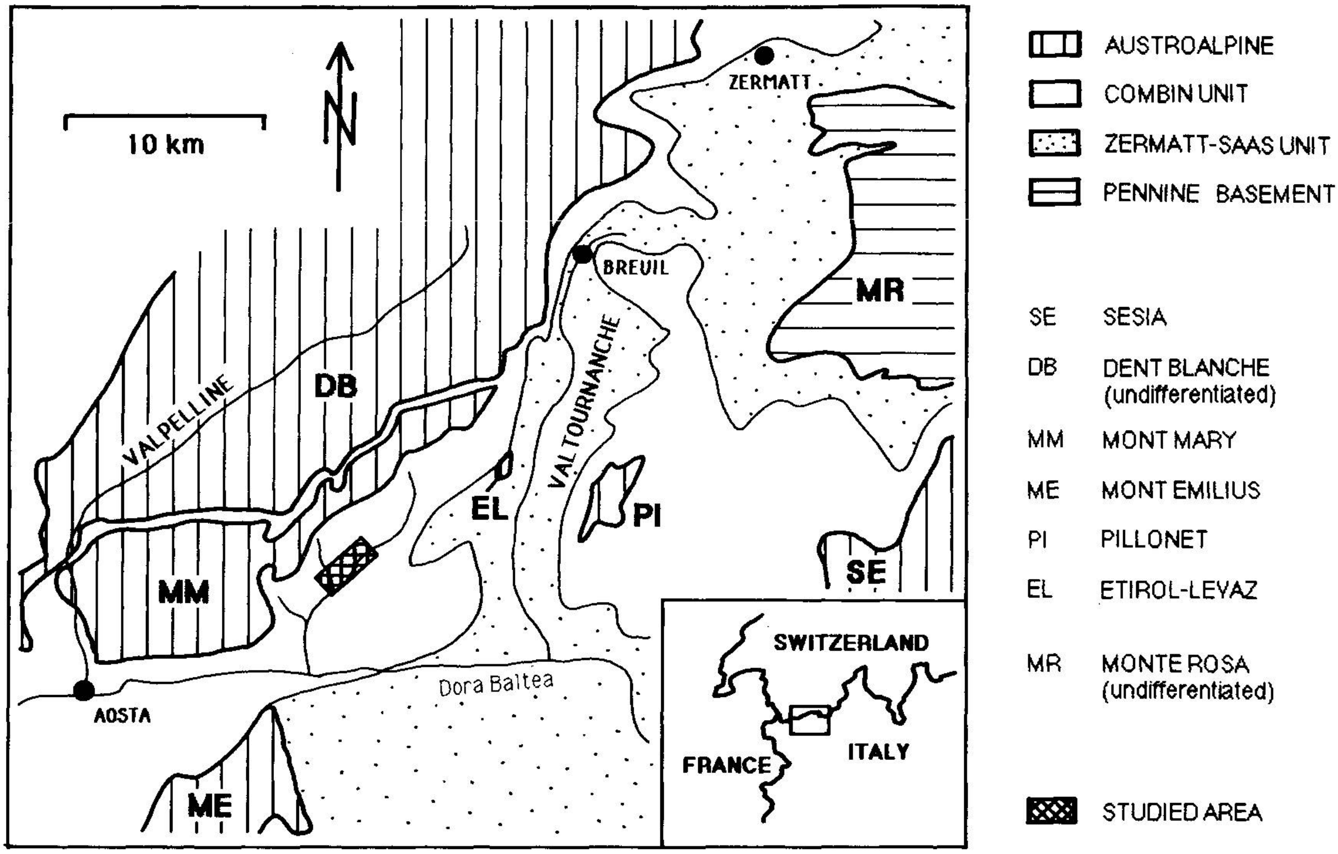

Fig. 1 Simplified tectonic map and location of the studied area. (Compiled from: Tectonic Map of Switzerland, 1:500000; BEARTH, 1967; DAL PIAZ, 1971.)

derlying Pennine Monte-Rosa and Grand St. Bernard nappes and the overlying Austroalpine Dent-Blanche nappe. In the area of Zermatt and Breuil it may be divided into an internal and structurally lower Zermatt-Saas unit and a more external Combin unit (BEARTH, 1967, 1974, 1976; DAL PIAZ, 1971, 1974a, 1974b; DAL PIAZ and ERNST, 1978; MARTHALER, 1984):

1) The Zermatt-Saas unit is composed of ophiolite segments from the thin oceanic crust of the Mesozoic Tethyan basin, i.e. serpentinized peridotites, metagabbros, metabasalts and to a lesser extent, of a typical Upper Jurassic to Cretaceous sedimentary cover. Eclogites and glaucophane schists give evidence of an eo-Alpine high-pressure event, with strong overprinting by Mesoalpine greenschist assemblages.

2) The Combin unit is dominated by sediments of continental-margin affinities comprising Upper Triassic to Cretaceous quartzites, marbles and calcschists. Ophiolitic fragments form layers up to 100 m thick of prasinites and ovardites (probably former basaltic lavas, tuffs and tuffites), as well as lenses of serpentinites and ophicarbonates. Eclogitic and blueschist assemblages are lacking, and, therefore, only greenschist metamorphic conditions have been attributed so far to this unit.

At least three phases of deformation (D1–D3) lead to a very complex structural situation in these two subunits (MILNES et al., 1981; MÜLLER, 1983; MAZUREK, 1986). Accordingly, their boundaries show complex imbrication tectonics as well, with the eclogitic Austroalpine 'klippe' of Etirol-Levaz lying sandwiched between them (BALLEVRE et al., 1986). Their distinction (e.g. by the appearance of high-pressure parageneses) is increasingly difficult towards the south.

The studied formations are considered to belong to the uppermost part of the Combin unit for the following reasons (after BEARTH, 1953, 1976; DAL PIAZ, 1969; DAL PIAZ and ERNST, 1978; MARTHALER, 1984; SPERLICH, 1986):

- eclogitic parageneses, clear ophiolitic sequences, and relics of pillow lavas are lacking

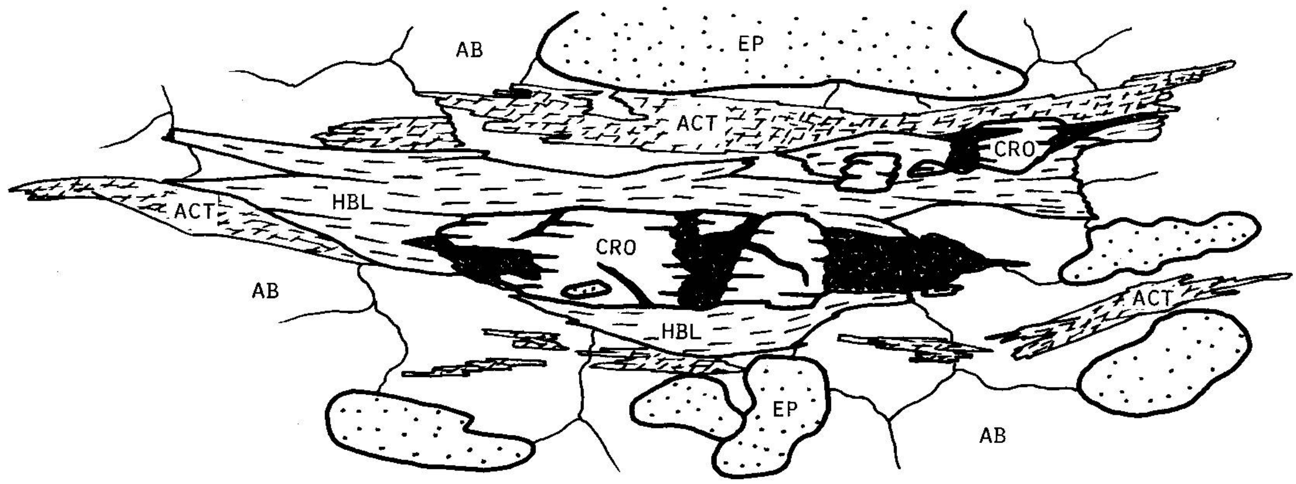

Fig. 2 Simplified textural relationships of described minerals in an epidote-rich prasinite (sample SP 154). Other phases are omitted by reasons of clearness. The fine-grained matrix consists mainly of biotite and chlorite and is concentrated only around crossites.
Abbreviations: Ab = albite; Act = pale-green actinolite; Cro = blue crossite; Ep = epidote; Hbl = blue green to green barroisite and hornblende.

- sedimentary lithologies predominate
- Mn-rich quartzitic schists are interbedded with serpentinites and calcschists
- Triassic sequences have not been observed

The possibility that the amphibole-bearing rocks of the area are imbricated parts of the underlying Zermatt-Saas unit cannot be absolutely excluded, although this seems improbable, due to the relatively high tectonic position (near the Dent-Blanche thrust fault) and the widespread appearance of these rocks.

Petrography

In St. Barthélemy four lithologies, in which blue amphiboles show different degrees of modification can be distinguished:

a) *Prasinites and ovardites* (metabasites) occur in layers up to 100 m thick, often intercalated with calcschists. These metavolcanic successions show characteristic greenschist assemblages with albite, epidote, chlorite, phengite as major phases, and amphiboles, biotite, quartz, magnetite, sphene, ilmenite (with armoured rutile), tourmaline, apatite as minor phases. Relictic amphibole grains may be preserved as inclusions in poikiloblastic albites or strongly altered into biotite and/or chlorite in epidote-rich rocks. They are usually scarce in specimens showing abundant albite crystallization (ovardites), a feature which is locally very variable. The amphibole content varies between 0 and 10 volume %. Commonly many amphibole types occur together, including crossite (blue/lilac), barroisite (blue-green), hornblende (green) and actinolite (pale green).

In the epidote-rich prasinites amphiboles occur in two different textures (see Figure 2). Crossites (texture 1) are aligned in an axial plane schistosity (Sl) and have a maximum length of 2.5 mm. They contain inclusions of rutile and epidote, show frayed edges, and are surrounded by a very fine-grained mixture of biotite, chlorite and magnetite, or are completely armoured by albite.

Blue-green, green and pale green amphiboles (texture 2) clearly post-date crossites (Fig. 2). They occur in fine bands, slightly bent

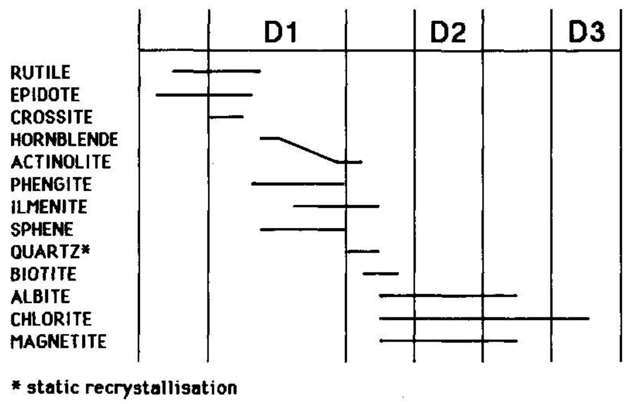

Fig. 3 Prasinite crystallization sequence with three deformation events. See text for further explanations.

around crossites and epidotes, but have the same orientation as crossites (Sl). Occasionally, they show a breakdown to chlorite and albite. Their different colours merge into each other without clear discontinuity which indicates a continuous compositional variation in this second group of amphiboles instead of coexisting equilibrium phases. The growth of actinolite at the expense of crossite can be modelled by the reaction

Crossite + epidote = actinolite + albite + chlorite + magnetite.

Fig. 3 shows the crystallization sequence for the evolution of epidote-rich prasinites in relation to deformation events (D1-D3). Rutile and early epidote may be relics of an oceanic metamorphic assemblage, preceding a long-lasting D1 phase with isoclinal folding and formation of an axial plane schistosity (Sl). Epidote, phengite and ilmenite partially coexisted with both textural types of amphiboles, before sphene and green to brownish-green biotite appeared. Static recrystallization of quartz is post-D1. Albite, magnetite and chlorite formed pre-D2 and syn-D2. It follows that albites, which always contain inclusions of both amphibole textural types and epidotes, have been partly deformed during D2 ('backfolding'), which took place under decreasing metamorphic conditions. D3 shows a semi-brittle style

Tab. 1 Representative microprobe analyses of minerals in epidote-rich prasinites.

SAMPLE	SP 154	SP 154	SP 154	SP 154	SP 154	SP 154	SP 154	SP 154	SP 154	SP 173	SP 173
MINERAL	CROSSITE	BARROIS	Mg-HOBL	ACT.HOBL	ACTINOL	PHENGITE	BIOTITE	CHLORITE	ALBITE	EPIDOTE (core)	EPIDOTE (rim)
SiO_2	56.51	48.49	48.11	50.15	53.17	49.61	37.21	27.01	68.85	35.21	37.17
Al_2O_3	7.09	6.68	7.12	5.86	2.47	26.24	14.93	19.88	19.29	20.56	23.17
Cr_2O_3	0.00	0.08	0.17	0.16	0.08	0.10	0.00	0.00	0.00	0.06	0.30
TiO_2	0.11	0.00	0.08	0.00	0.00	0.25	1.27	0.04	0.04	0.37	0.07
Fe_2O_3*										19.55	13.36
FeO **	16.15	19.30	16.82	16.38	12.61	4.33	16.55	19.47	0.06		
MnO	0.00	0.34	0.29	0.21	0.26	0.06	0.26	0.28	0.00	0.17	0.08
MgO	9.82	9.56	11.62	12.26	15.96	2.94	12.40	20.12	0.00	0.24	0.11
CaO	0.65	7.37	8.69	8.54	11.38	0.07	0.29	0.00	0.00	22.00	22.91
Na_2O	6.53	3.35	2.90	2.68	0.99	0.32	0.06	0.00	11.72	0.00	0.00
K_2O	0.01	0.21	0.25	0.18	0.05	10.27	9.38	0.00	0.00	0.00	0.00
TOTAL	96.87	95.38	96.05	96.42	96.97	94.26	92.35	86.80	99.96	98.16	97.17
FORMULAS											
OXYGENS	23.0	23.0	23.0	23.0	23.0	22.0	22.0	28.0	8.0	12.5	12.5
Si	7.891	7.236	7.080	7.297	7.620	6.774	5.780	5.572	3.005	2.867	2.986
Al	1.168	1.176	1.236	1.006	0.418	4.223	2.734	4.834	0.992	1.973	2.194
Cr	0.000	0.009	0.020	0.018	0.009	0.011	0.000	0.000	0.000	0.004	0.019
Ti	0.012	0.000	0.009	0.000	0.000	0.012	0.148	0.006	0.001	0.023	0.004
Fe^{3+}	1.063	0.976	0.952	0.929	0.555					1.198	0.807
Fe^{2+}	0.822	1.432	1.117	1.063	0.956	0.477	2.150	3.358	0.002		
Mn	0.000	0.043	0.036	0.026	0.032	0.000	0.034	0.049	0.000	0.012	0.005
Mg	2.045	2.128	2.550	2.660	3.411	0.627	2.871	6.186	0.000	0.029	0.013
Ca	0.097	1.178	1.370	1.331	1.747	0.013	0.048	0.000	0.000	1.919	1.971
Na	1.768	0.969	0.827	0.756	0.275	0.085	0.018	0.000	0.992	0.000	0.000
K	0.002	0.040	0.047	0.033	0.009	1.832	1.859	0.000	0.000	0.000	0.000

* total Fe as Fe_2O_3

** total Fe as FeO

Redistribution of total Fe in amphiboles after LEAKE (1978), ROCK and LEAKE (1984) of deformation below greenschist temperature (SPERLICH, 1986).

b) *Carbonate-rich lenses* of some centimeters appear within these prasinites. They consist mainly of calcite, epidote and chlorite with minor phengite , albite, amphibole, biotite, sphene, rutile, hematite, magnetite, tourmaline and apatite. In contrast to the surrounding prasinitic rocks (containing crossites), the sodic amphiboles of these lenses are glaucophanes (Fig. 4a), showing a lower degree of alteration. They are partially pseudomorphed by fine-grained green biotite and minor chlorite. Younger amphiboles do not exist in these carbonate-rich lenses.

c) Meter-thick layers and slabs of *epidote-actinolite-schists* contain as minor constituents calcite, chlorite, garnet and accessories. Ilmenite and dolomite occur only as armoured relics in garnets, and crossite flakes are preserved within garnets and epidotes.

d) Very massive *chromium-bearing epidote-quartz rocks* form local rounded lenses of meter-dimensions within quartzitic micaschists. They attract attention in the field by their dark brown colour due to chromium-rich epidotes (1-3% Cr) and the appearance of green fuchsite. Besides epidote, quartz and/or dolomite, the minor constituents are chlorite, albite, sodic amphibole (not analysed), fuchsite, biotite, ilmenite and accessory rutile and garnet. Amphiboles show blue to lavender pleochroism and are concentrated in fine horizons forming a compositional layering. They may be altered into biotite and/or overgrown by albite. Some blue-green amphiboles appear occasionally.

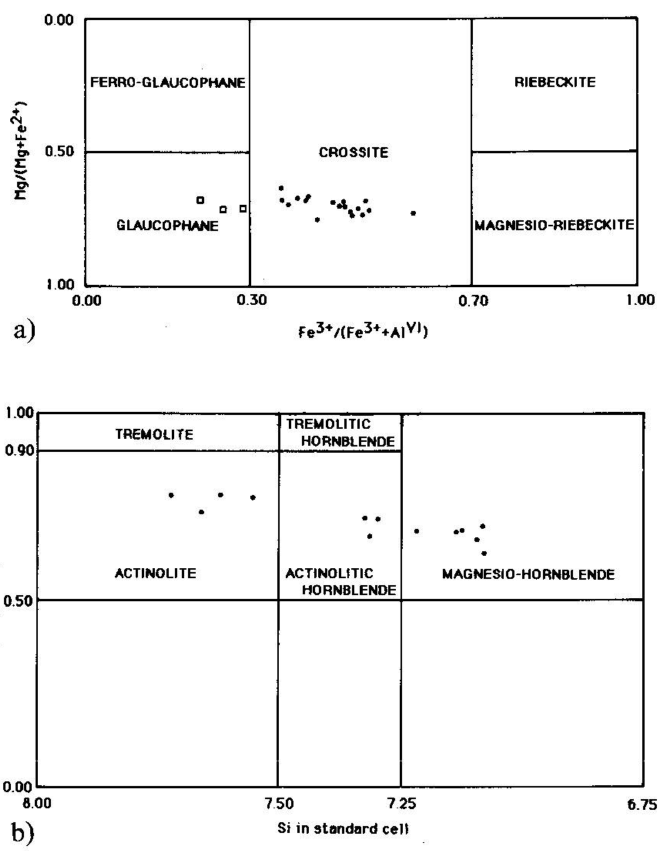

Fig. 4 Amphibole classification schemes after LEAKE (1978)

a) sodic amphiboles:
   dots: crossites from an epidote-rich prasinite (SP 154)
   squares: glaucophanes from a carbonate-rich lens (SP 173)

b) calcic amphiboles:
   variation from Mg-hornblende to actinolite (SP 154).

Mineral chemistry and compositional trends

One epidote-rich prasinite sample with a low grade of albite crystallization has been chosen for detailed investigations (SP154). Amphibole formulas were calculated on an anhydrous basis of 23 oxygens. Fe^{3+}-contents of amphiboles have been determined after ROCK and LEAKE (1984), and names are given using the nomenclature scheme of LEAKE (1978). Representative analyses for different amphiboles, epidote (core-rim), phengite, biotite, chlorite and albite are listed in Table 1.

Epidotes show an increase in Al from core to rim with X(Clz) ranging from 0.0 to 0.19. Sample SP173 is given instead of SP154 for epidote analyses in Table 1 due to insufficient data for the latter specimen. In phengites, about 1 octahedral Al is replaced by Mg and Fe per unit cell. Biotite has a mean Mg/(Mg+Fe) ratio of 0.58 and chlorite varies between ripidolite and pycnochlorite (after DEER et al., 1962). Albites have almost end-member composition with X(Ab) ranging from 0.99 to 1.0.

Amphiboles with blue to lilac pleochroism are crossites with a $Fe^3/(Fe^{3+}+Al)$ ratio ranging from 0.595 to 0.357 (see Fig. 4a). With the exception of one barroisite (not plotted in Fig. 4), blue-green , green and pale green amphiboles show a systematic compositional trend from barroisite to Mg-hornblende, actinolitic hornblende and eventually actinolite (see Fig. 4b). A systematic decrease in Na(tot)

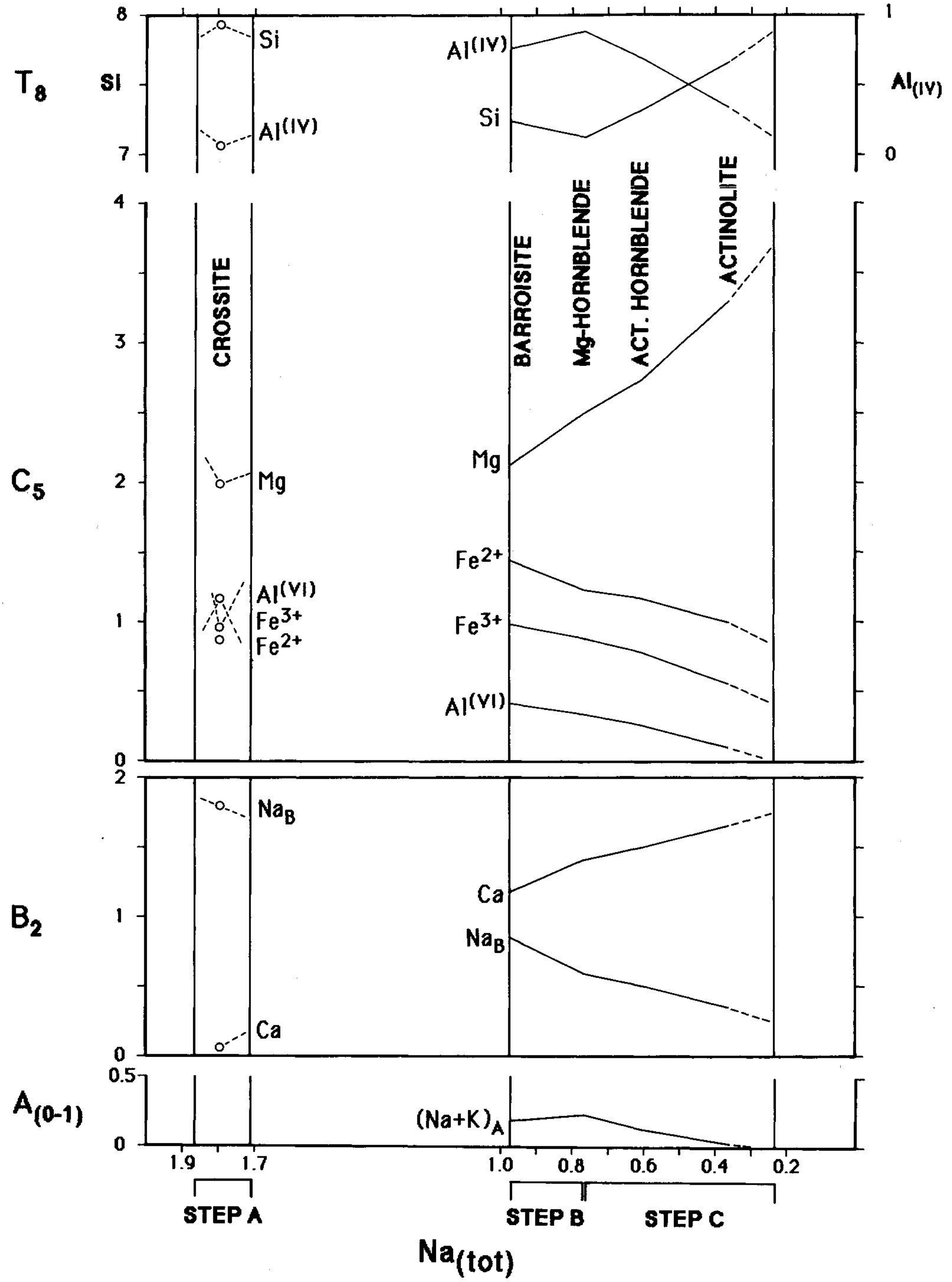

Fig. 5 Compositional trends in amphiboles: $A_{0\text{-}1}\ B_2\ C_5\ T_8\ O_{22}\ (OH)_{22}$, plotted against $Na_{(tot)}$ with respect to structural sites. Steps A, B and C indicate ranges of analysed $Na_{(tot)}$-values with different compositional trends. Note the gap between crossite and barroisite.

- dashed lines in step A: qualitative trends in crossite single-grains, added to mean values (open circles)
- dashed lines in step C: best fit line from mean actinolite to lowest $Na_{(tot)}$
- solid lines: connected mean values of different amphiboles.

from core to rim was observed in single crossite grains. This decrease even continues from barroisites to (younger) actinolites. Thus the total Na content serves as an indicator of successive growth stages. In Fig. 5, mean values of the main elements are plotted versus Na(tot) for each type of amphibole (defined in Fig. 4). Compositional trends during the growth of amphiboles are established by connecting these mean values in Fig. 5.

The first generation of amphiboles are crossites with Na(tot) = 1.70–1.85 p.f.u. (= STEP A). Single grains display some compositional trends; but there is, however, a larger variation of composition between different grains. Due to this fact and the small number of available single grain data, trends within crossites are marked with dashed lines in Fig. 5.

A large composition gap (Na(tot) = 0.97–1.70 p.f.u.) separates crossites from barroisites. This common feature will be discussed in the following section.

The transition from barroisite to actinolite is divided into two steps which are solely defined by compositional criteria. STEP B is characterized by an increase of tetrahedral Al at the expense of Si, and a decrease of A-site vacancies, filled by Na and K. In STEP C Si, Mg and Ca increase continuously, whereas the other main elements decrease.

Approximated substitution vectors are listed in Table 2. They have been evaluated from slopes of connecting lines between mean values of each element (see Fig. 5). No attempt has been made to quantify crossite trends for the reasons mentioned above: exchanges of Fe^{3+} for Al(VI) and Ca + Al(IV) for Na + Si are obvious, while variations in the Mg/-(Fe^{2+} + Mg) ratios are insignificant.

Discussion

The succession sodic amphibole-barroisite-actinolite is ubiquitous in metabasites of the western Alps, and reflects the change from blueschist to greenschist conditions (BEARTH, 1959, 1973; CORTESOGNO et al., 1977; DAL PIAZ and ERNST, 1978; ERNST and DAL PIAZ, 1978; ERNST, 1979; DAL PIAZ and LOMBARDO, 1986; DEN TEX, 1987).

The growth of glaucophane and crossite within different horizons only a few centimeters apart (SP173), indicates that the glaucophane content in sodic amphiboles is not only dependent on P-T conditions (WOOD, 1980), but also controlled by the bulk composition of the host rock (COLEMAN and PAPIKE, 1968; BROWN, 1974). Experimentally determined

Tab. 2 Balanced substitution coefficients in different steps of amphibole-growth, deduced from mean values in Fig. 5. 1 O refers to 1 kation or vacancy (□) in $A_{0\text{-}1}\,B_2\,C_5\,T_8\,O_{22}\,(OH)_2$.

	DECREASE				INCREASE			
STRUCTURAL SITE	A	B	C	T	A	B	C	T
STEP A * (crossite)		Ca	Fe^{3+}	Al		Na	Al	Si
STEP B (barroisite-Mg-hornblende)	$Na_{.05}$	$Ca_{.2}$ $Ca_{.05}$	$Mg_{.2}$ $Mg_{.2}$	$Al_{.1}$	$□_{.05}$	$Na_{.2}$ $Na_{.05}$	$Fe^{2+}_{.2}$ $Fe^{3+}_{.1}$ $Al_{.1}$	$Si_{.1}$
STEP C (Mg-hornblende-actinolite)	$□_{.3}$	$Ca_{.3}$	$Mg_{.3}$ $Mg_{.4}$ $Mg_{.4}$	$Si_{.3}$ $Si_{.4}$	$Na_{.3}$	$Na_{.3}$	$Fe^{3+}_{.3}$ $Al_{.4}$ $Fe^{2+}_{.4}$	$Al_{.3}$ $Al_{.4}$

* only qualitative

minimum pressures for sodic amphiboles show pronounced variations and significant dependence on the Fe content in the model system (MARESCH, 1977; KOONS, 1982; CARMAN and GILBERT, 1983; MARUYAMA et al., 1986). Oxygen fugacity is also an important factor influencing reactions at the blueschist-greenschist boundary (BROWN, 1974; GIBBONS and GYOPARI, 1986). In any case, the occurrence of these sodic amphiboles with epidote and rutile as remnants of a first metamorphic event points to higher pressures than expected for common greenschist conditions.

A compositional gap between coexisting sodic amphiboles and barroisite with a solvus has been reported from numerous occurrences (e.g. COLEMAN and PAPIKE, 1968; KLEIN, 1969; WETZEL, 1974; GIBBONS and GYOPARI, 1986; LIOU and MARUYAMA, 1987). This solvus seems to close under conditions approaching 400 °C and 7 kbars (ERNST, 1979). Therefore, these amphiboles probably represent a non-equilibrium pair, as confirmed by their textural relationship. No compositional gap has been observed within calcic amphiboles, and a gradual transition must be assumed rather than equilibrium coexistence.

The Al_2O_3 content of crossites from this study requires empirically determined pressures of 5.6 to 6.3 kbars after MARUYAMA et al. (1986). The glaucophane content in these crossites gives a lower stability limit of 5 to 6 kbars after DE ROEVER and BEUNK (1976). Assuming temperatures of around 400 °C, barroisite appears to be stable at minimum pressures of 4.5 to 6 kbars, and reflects a product of decompressive recrystallization in the Valtournanche area (ERNST, 1979). Mg-hornblende grew at the stage of maximum temperature as it has highest Al(IV) content, whereas the following transition to actinolite with a systematic decrease in Na, Al, and Fe indicates retrogressive conditions (BLACK, 1977; WETZEL, 1974). The Na(M4) content in the analysed amphiboles suggests pressures of about 7 kb for barroisites, 6 kb for hornblendes and 3 kb for actinolites after BROWN (1977). The reaction characterized above

crossite + epidote = actinolite + albite + chlorite + magnetite

is similar to the one described by BROWN (1974) for actinolite growth at the expense of crossite (with intermediate Fe content) at the blueschist-greenschist transition around 3–4 kbars.

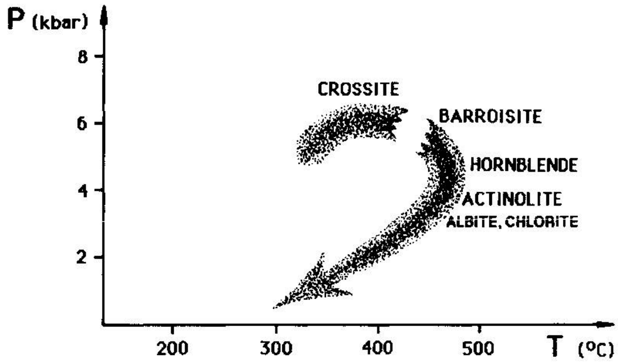

Fig. 6 Metamorphic evolution of Combin metabasites with indicated amphiboles and main prasinite-forming minerals albite and chlorite.

A tentative new P-T-path for Combin metabasites is suggested in Fig. 6, beginning with lower blueschist conditions. A thermal re-equilibration to maximum temperatures of around 450 °C (e.g. DAL PIAZ and ERNST, 1978; ERNST and DAL PIAZ, 1978; DAL PIAZ and LOMBARDO, 1986; MAZUREK, 1986) is followed by gradual retrogressive evolution.

Conclusions

- Crossites appear as relics of a first regional metamorphic event in Combin metabasites at lower blueschist conditions.
- After a break in amphibole growth, barroisite and Mg-hornblende formed during a temperature increase and a beginning pressure decrease.
- At the beginning of the retrogressive evolution, amphibole composition changed from Mg-hornblende to actinolitic hornblende and actinolite. During a last phase, quartz recrystallized, and albite, chlorite and magnetite appeared, forming prasinites and ovardites.
- The whole metamorphic evolution is regarded as a continuous process with a pressure dominated early stage as it is characteristic for Pennine units west of the Lepontine region.
- The Combin unit as the upper part of the Piemont ophiolite nappe may have been partially subducted, but to shallower depths than the Zermatt-Saas unit. The greenschist facies overprint has affected the whole nappe pile after its general emplacement.

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